

COMMERCIAL OXIDATION
OF GERANIOL TO GERANIAL

BY

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ARMOUR INSTITUTE OF TECHNOLOGY

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Commercial oxidation of
geraniol to geranial

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COMMERCIAL OXIDATION OF GERANIOL TO GERANIAL

A THESIS

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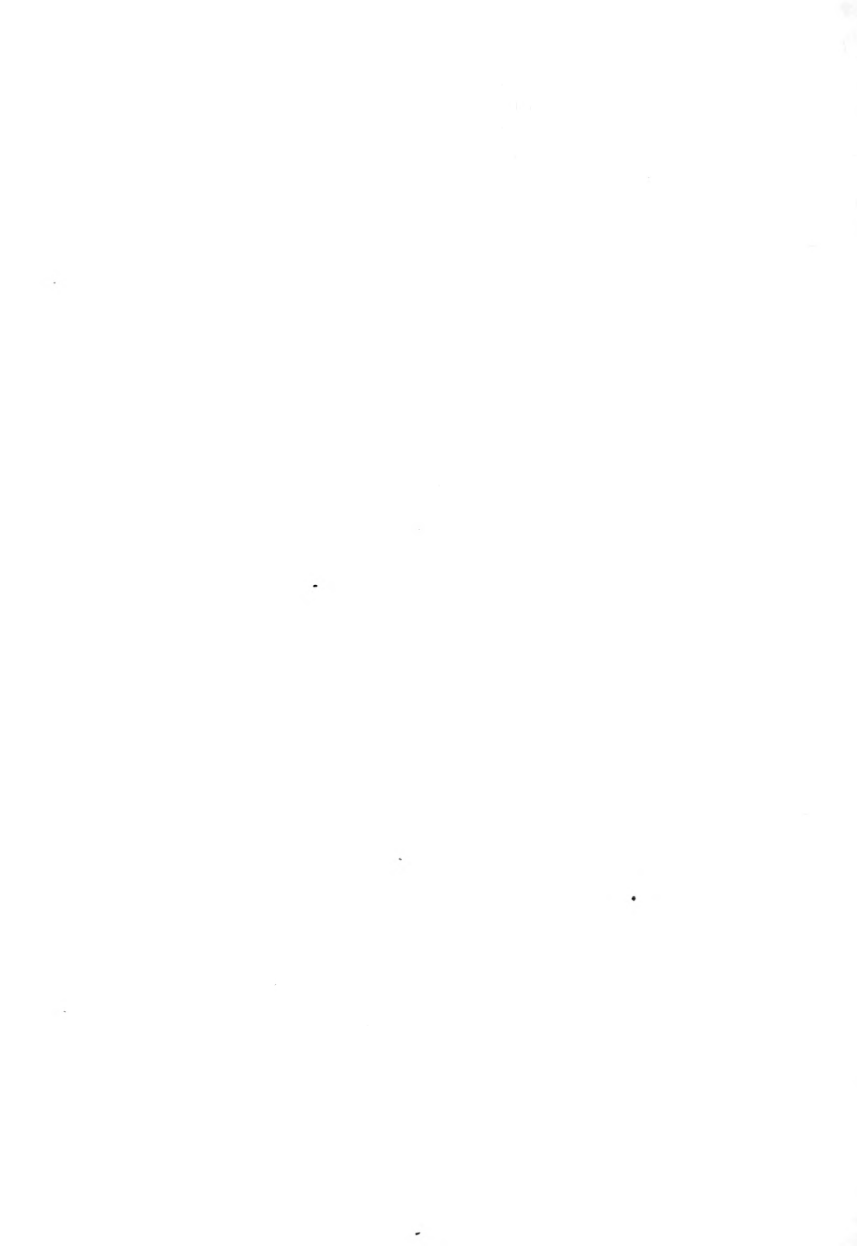


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THE COMMERCIAL OXIDATION OF GERANIOL TO GERANIAL

The subject of artificial or synthetic perfume is of surpassing interest and importance to the practical perfumer as he is constantly confronted with the consideration of synthetics, new and old, and their usefulness and practical value as compared with natural products. In particular, the saving of expense made possible by their use is sufficient to warrant their employment wherever possible. In order to comprehend their real field of usefulness, it is first necessary to ascertain where the line between natural and synthetic products should be drawn.

By natural products are meant those which are directly drawn from flowers, leaves, roots, herbs, fruits, etc., whether by expression, distillation, maceration, or extraction by volatile solvents.

By what are known as synthetic products are meant those products which are obtained from a natural base by chemical treatment or by combination of one or more organic or inorganic chemicals to produce the aromatic or odorous bodies. The resulting combinations are more or less contaminated with impurities. These are removed by purification and it is on the care and skill with which this purification is effected that the quality and odor value of the synthetic depend.

It should be borne in mind that many of the synthetics are made indirectly from vegetable bases, for example: Heliotropin from oil of camphor, vanillin from oil of cloves, terpineol from oil of turpentine, the artificial violets from oil of lemon-grass. These few instances of products so universally used should serve to dispel the general misconception that most of the synthetics are coal-tar derivatives.

Nothing was ever further from the truth, as any perfume chemist knows, yet it is often difficult to correct this false conception. It is therefore plain that there is some overlapping of the natural products and the synthetic, in those instances in which the synthetic is derived from vegetable bases, but where this derivation is only a metamorphosis of the needed chemical elements, and not of the odorous principle on a whole, they may be termed synthetic.

It may be primary to say that synthesis in this field, as in all chemistry, is based upon analysis, but it is most necessary to emphasize this if the proper understanding is to be had. It was only after the pure natural products had been carefully analyzed and their elements found that it was possible to search for their elements in other less costly substances of vegetable or mineral origin and recombine them into artificial aromatics, resembling the compounds

sought to be reproduced. And yet, up to the present time, this work of analysis and synthesis leaves much to be desired. Not yet has it proved practical to imitate the delicate chemistry of nature in all of its infinite detail, and for this very reason it is not yet possible, if it ever will be, to reproduce scientifically and successfully, all of the characteristic qualities of any natural product.

In fact, it seems as if the natural and synthetic perfume materials supplant one another most happily. It is a provable fact that in the process of extracting natural products some important odorous elements are lost, and it is these missing notes necessary to the complete chords of the odorous harmony which are sometimes supplied by well-made synthetics. It is indisputable that many synthetic products often intensify the odors of the nat-

ural products. The development of artificial perfumers' materials has made possible the manufacture of many new and novel odors, as well as the perfecting of the old staple odors. Concurrently with the marked advance made by the manufacturers of synthetics during the last twenty years or so, the manufacturers of the natural products have also progressed. They have expended fortunes upon experiments in fertilizing the soil, crossing of types, and the grafting of plants, at the same time that they have perfected their methods of distillation and extraction, heightened the efficiency of their machinery, and secured the ripest results of expert chemical aid, so as to secure all that was possible from the crude materials; and by the discovery of new solvents they have succeeded in obtaining products of great strength and purity. In this way the wide use of synthetics has had an excellent effect in stimulating the

manufacturers of the natural products to improve their processes in every direction.

Regardless of the fact that the consumption of synthetics has increased enormously, as they deserved to increase with the spread of knowledge and appreciation of the value of these important ingredients, it would be taking an unwarranted liberty to state that the synthetics can replace the natural products. These are still the real basis of good perfumery, and are just as necessary as ever for the attainment of many perfume effects which are impossible otherwise. In the proper combination of the natural and synthetic products, based upon clear understanding of the proper functions of each in the economy of the perfume industry, lies the best guarantee of success. Each have its work to do; neither is complete without the other, and working harmoniously the results will be both rich and satisfying.

As has been said before, until recent years very little work has been done along the development of the chemistry of the synthetic perfumes. Heretofore the so-called volatile oils were used as perfumes. Later it was found that the odor was due to one of the constituents of the oil. These constituents were then identified and their structure determined. Since their identification several attempts have been made to synthesize these bodies. At first the efforts of synthesizing these bodies were fruitless, but recently their efforts have not been in vain for a few perfumes have been successfully synthesized and are being manufactured on a semi-commercial scale with very little difficulty. The essence of violets is one of those that is not produced very successfully commercially. It gives great promise of being successfully produced, however, sometime in the near future due to the efforts of some American chemists. The essence of violets

is a mixture of a- and b-ionone. By the condensation of acetone and geranial in the presence a catalyzer pseudo-ionone is formed. This, on treatment with any acid as sulphuric, hydrochloric, phosphoric, etc., transforms into a- and b-ionone.

Ionone has an intensely powerful odor which gives a delightful violet perfume when sufficiently reduced in strength. For handkerchief perfumes it may be used in full strength in proper quantities and providing there is sufficient liquid content to provide suitable dilution, but for perfuming creams and similar toilet preparations a solution of 1%, that is, 1 dram of ionone of 100 drams of alcohol, should be made and a few drops of this used to suit.

The perfume of the violet, *viola odorata*, is due to a volatile oil of a green color and of such penetrating odor as to cause headaches; it acquires the agreeable odor of the violet only by strong dilution. The violet farms from whence the flowers are

procured for the production of the oil, are very extensive at Nice and in the neighborhood of Florence. The oil can only be obtained by the absorption process, all other methods of procuring it having failed up to the present time. It is scarcely obtainable in commerce as the French manufacturers, who prepare the greater part of it use the very small yield for the manufacturing of fine perfumes. This is the most costly of all perfumes, for the plant is small and the flowers few and it requires a good deal of space and labor in its cultivation, and also because it is but a short time in bloom. All these items tend toward an increase in the cost of production.

A few patents have been taken out for the production of ionone by the condensation of geranial and acetone in the presence of alkaline-earth hydrates. In all the patents it seems that the geranial was obtained from the essent-

ial oil of lemon-grass. None of the specifications of any of these patents have ever been attempted for commercial advantage. This was due to the fact that the amount of geranial present in the oil of lemon-grass was not a sufficient quantity to make the operation commercially feasible. It is for this reason that I have tried to produce the geranial by the oxidation of the corresponding alcohol geraniol. This alcohol is so abundant in most all of the essential oils that I am sure a cheap source of supply can be found. If this is accomplished it will make the synthesis of the oil of violets a commercial success.

The geraniol used for this work was supplied by the Kenart Synthetic Products Company. The analysis of the reaction mixtures in unsuccessful attempts at oxidation were performed in the laboratory of the aforementioned chemical company.

THE TIEMANN AND SEMMLER PROCESS

This process which has been proven to have nothing but a purely theoretical significance is as follows:-

For the oxidation of geraniol to geranial ten grams of potassium bichromate are dissolved in one hundred grams of water containing twelve and one half grams of sulphuric acid. To this, fifteen grams of geraniol are added all at once, the mixture being at first kept well cooled, and afterwards allowed to become warm. The reaction mixture is subjected to vigorous stirring during the cooling operation. The whole is then made slightly alkaline with sodium carbonate and distilled in a current of steam. The distillate contains an oil which has a pleasant odor resembling oranges and lemons, and is a mixture of the oxidation product with ethereal oils formed by the action of the sulphuric acid on

the geraniol. To separate the latter the oil is mixed with a saturated solution of sodium hydrogen sulphite, and allowed to stand for twenty four hours. The crystalline magma is then collected, pressed between filter papers, washed with ether, mixed with sodium carbonate and distilled in a current of steam. A clear colorless oil, having the composition $C_{10}H_{16}O$ and the above mentioned characteristic odor, is obtained.

Two preparations similar to the above mentioned process were worked through and although there was complete reduction of the bichromate there was very little geranial produced. In both of these attempts a determination of the geranial content was made, the method of which will be taken up later, and between six and eight percent of the theoretical is all that could be found. This without a doubt proves that the Tiemann and Semmler process could not

be used as a practical method with any very great commercial success. The great difficulty in this method lay in the fact that a superfluous amount of tarry resinous matter was formed. These two reaction mixtures were analysed and besides the resins, acetic capronic, myristic, and valerianic acids were found along with some esters of these acids. This shows that the oxidation was too strong, that is, it broke up the unsaturated alcohol at the ethylene linkages.

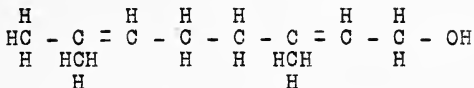
After steam distillation the solutions were mixed with a saturated solution of sodium bisulphite and allowed to stand for twenty four hours as directed in Tiemann-Semmler's process. At the end of this time there was no crystalline magma as prescribed in the directions. To one of these I tried "salting out" the crystalline compound by the addition of solid sodium chloride, but with no success. To the other I

added benzol so as to dissolve the geranial out of the solution if any were present. Upon the evaporation of the benzol it was found to contain no geranial.

CHEMISTRY

GERANIOL

2,6 Dimethyl-octadiene 2,6 (ol) 2



Geraniol is distinguished from other members of the geraniol-citronellol family by its optical inactivity, higher boiling point and higher specific gravity. It is the "lemonol" of Barbier Bouveault, and the "rhodinol" of Erdmann and Huth and of Poleck. Both as such and as ester it is found rather frequently in volatile oils. It constitutes the bulk palmarosa oil, of German and Turkish rose oils, and is found in appreciable quantities in the oils of geranium, citronella, and lemon-grass. It has further been found in the oils of gingergrass, Canada snakeroot, ylang-ylang, champaca flowers, Eucalyptus Macarthuri, and several other oils. As acetate it occurs in

the needle oil of *Callitris glauca* and a few others. It also occurs as valerianate, capronate, and tiglate. It is thus the most important alcoholic constituent of this group of essential oils.

As a primary alcohol, geraniol forms a crystalline addition product with calcium chloride, which is insoluble in ether, ligroin, benzene and chloroform, and which is resolved into its components by water..

For the isolation of geraniol from mixtures with hydrocarbons and other substances a number of other methods have been suggested. All of them have this in common that they aim at the preparation of an acid phthalate of geraniol. This ester can be prepared either by the action of phthalic acid anhydride on the sodium compound of crude geraniol, or by heating geraniol with phthalic acid anhydride without solvent on the water bath or in benzene solu-

tion. The ester can be purified through the crystalline silver salt. The geraniol is regenerated by saponifying either the acid ester or its sodium salt. These methods, however, do not possess any advantages over the calcium chloride method. Indeed they are more complicated and yield no purer product.

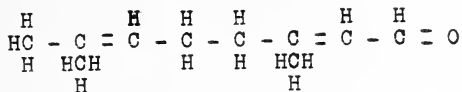
Purified geraniol, prepared by one or the other of the above methods, is a colorless, oily liquid with a rose-like odor which is optically inactive. In connection with products prepared by themselves on a large scale Schimmel and Company observed the following properties:

Boiling point, 229 to 230° at 757 mm., 114 to 115° at 12 mm., density, 0.883 to 0.886 at 15 degrees; its refractive index is 1.476 to 1.478 at 20 degrees; soluble in 8 to 15 volumes of 50 percent alcohol and in 2.5 to 3.5 volumes of 60 percent alcohol.

Upon oxidation geraniol, as a primary alcohol, yields geranial, from which it can be obtained by reduction with sodium amalgam. Under special conditions, however, methyl heptenone can also be obtained. Other "Abbau" products are likewise obtained, so that the reaction is by no means a quantitative one.

GERANIAL

2,6 Dimethyl-octadiene 2,6(al)8



Geranial is the only aliphatic aldehyde of the general formula $\text{C}_{10}\text{H}_{16}\text{O}$ that has thus far been isolated from volatile oils. Its occurrence in nature is rather common. It was first found by J. Bertram in the oil of *Bockhousia citriodora*. Larger amounts are contained in the lemon-grass oil than in the *Bockhousia* oil just referred to. It occurs also in Java citronella oil, ginger oil, kobushi oil, sassafras leaf oil, japanese cinnamon oil and several other common oils but in none does it occur in very large quantities.

From all the oils named above, geranial can be isolated by means of its crystalline addition product with bisulphite. From this compound, after previous purification by wash-

ing with alcohol and ether, geranial can be obtained in a pure state by decomposition with alkali carbonate. Synthetically geranial has been obtained by the distillation of the calcium salt of geranic acid with calcium formate.

Commercial products prepared by Schimmel and Company had the following properties:

Density of 0.892 to 0.895 at 15 degrees; refractive index of 1.488 to 1.489 at 20 degrees; soluble in about 7 volumes of 60 per cent alcohol.

As diolefinic aldehyde geranial adds two molecules of halogens. Towards acids and acid reagents it is very susceptible. Dilute sulphuric and potassium acid sulphate act very energetically with the formation of cymene. Alkalies likewise attack geranial. When boiled with potassium carbonate solution it is broken up into acetaldehyde and methylheptenone. Geranial reveals all the properties of an

aldehyde. It reacts with the well-known reagents for aldehydes and when reduced with sodium amalgam in acetic acid solution it is converted into geraniol. Toward sodium acid sulphite solution it behaves in a peculiar manner. If the solution does not contain too large an amount of free sulphurous acid, the difficultly soluble, normal crystalline addition product $C_9H_{15}CH(OH)SO_3Na$, is formed when the aldehyde is shaken with such a solution. From this compound sodium carbonate and sodium hydroxide regenerate the geranial but not quantitatively. If, however, this crystalline addition product is gently heated with an excess of bisulphite solution, it is dissolved with the formation of a "labile" dihydrodisulphonic acid derivative of geranial, $C_9H_{17}(SO_3Na)_2CHO$. From this the geranial can be regenerated only by means of caustic alkalies.

DISCUSSION OF RESULTS SHOWN IN TABLES

As can readily be seen from table I strong oxidizing agents will not give satisfactory results. Runs numbered 1 and 2 were made following the directions prescribed by Tiemann and Semmler. For some unknown reason they use only the theoretical amount of potassium bichromate needed for the oxidation. Two simultaneous runs of potassium chromate were made but these efforts only gave acetic acid as a primary product. Potassium chlorate was next used and it also was found to give acetic acid as a primary product. With nitric acid several products were formed, nitrobenzol being the predominating compound.

Table 2 shows the data and results of several different runs using potassium permanganate. Two individual runs with different dilutions of cold neutral permanganate were made. The acid was allowed to dribble in just fast enough to

keep the solution neutral. No analysis of the reaction-mixture was necessary because the disagreeable odor of valeric acid was predominant. Two similar runs of hot neutral permanganate were made and these gave acetic acid. Alkaline permanganate was next tried and it gave the same results as cold neutral permanganate.

Table 3 shows the data and results of acid permanganate which was then tried and found to give satisfactory results, that is, it gave some geranial. Four or five runs were then made with acid permanganate varying the dilution from 250 c.c. to 1 liter. Similar runs were made for acidity and excess of the permanganate and it was found that the best results were obtained when 7 grams of potassium permanganate were dissolved in 500 c.c. of water containing 7.5 grams of sulphuric acid. This will give results varying from 16 to 18 percent of the theoretical yield.

This yield was not quantitative enough for commercial application so it was decided to try changing the detailed manipulation of the bichromate process as outlined by Tiemann and Semmler. The first three runs of table 4 use the same quantities of bichromate and acid that Tiemann and Semmler used. The difference being that the acid solution of potassium bichromate was added to the geraniol gradually and with vigorous stirring, during the course of one hour and thirty minutes. In these three runs only the theoretical amount of potassium bichromate was used. Three different dilutions were tried, i.e., ten grams of potassium bichromate were dissolved in 100, 200, and 500 c.c. of water respectively. The ten grams dissolved in 200 c.c. of water was found to give the most satisfactory results. The other runs in the table were made increasing the percent of excess of potassium bichromate. An excess of from fifteen to

eighteen percent increases the yield materially. Beyond this point an increase in the amount of potassium bichromate used only tends toward a reduction of the yield of geranial. The reaction-mixture in all this work must be kept at a constant temperature of about 20 degrees centigrade.

TABLE I

RESULTS OF STRONG OXIDATION

No. of run	Oxidizer used	Grams used	Percent excess	Grams acid	C.C. H ₂ O	Yield in % theoretical
a1	K ₂ Cr ₂ O ₇	10	0.2	12.5	100	6.2
a2	K ₂ Cr ₂ O ₇	10	0.2	12.5	100	8.6
3	KCrO ₄	8.5	9.0	10.5	100	CH ₃ COOH
4	KCrO ₄	8.5	9.0	10.5	100	CH ₃ COOH
5	KClO ₃	9.0	13.1	7.0	100	CH ₃ COOH
6	KClO ₃	9.0	13.1	7.0	100	CH ₃ COOH
7	HNO ₃	15.0	83.0		200	C ₆ H ₅ NO ₂
8	HNO ₃	15.0	83.0		200	C ₆ H ₅ NO ₂

1 and 2 according to Tiemann's specifications

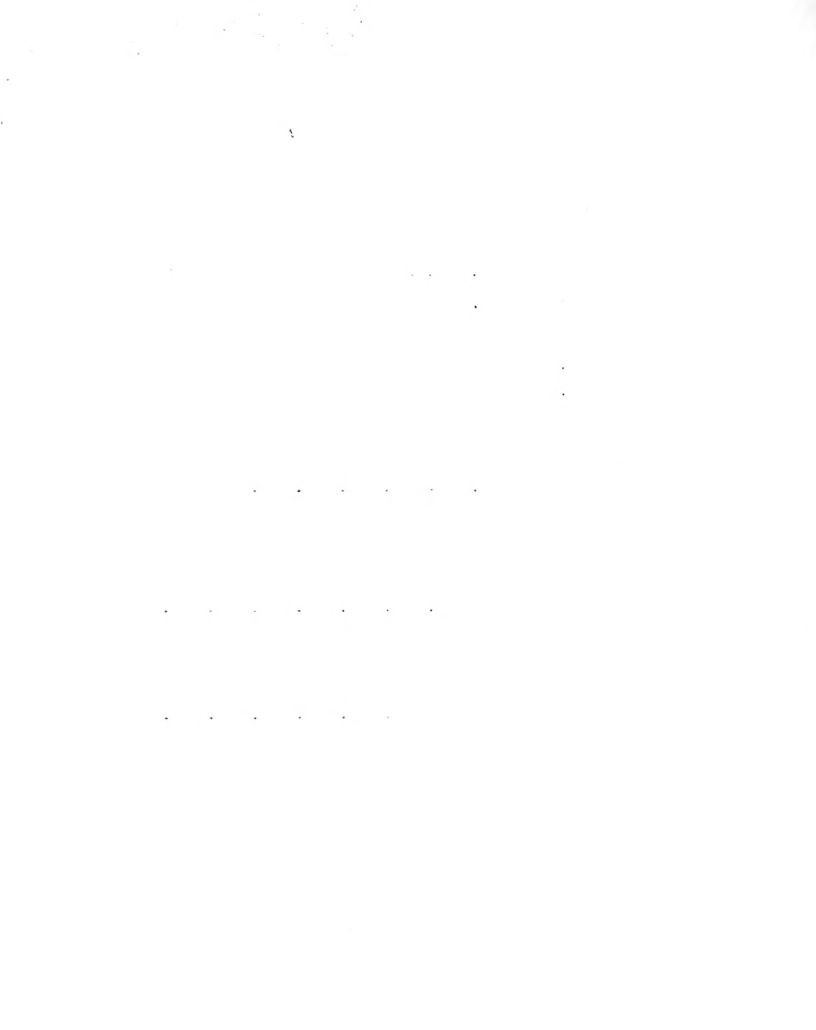


TABLE 2

RESULTS OF NEUTRAL AND ALKALINE PERMANGANATE

No. of run	Oxidizer used	Grams used	Percent excess	Grams acid	C.C. H ₂ O	Yield in % theoretical
a9	KMnO ₄	11.0	7.8	5.6	500	Valeric acid
a10	KMnO ₄	11.0	7.8	5.6	1000	Valeric acid
b11	KMnO ₄	11.0	7.8	5.6	500	CH ₃ COOH
b12	KMnO ₄	11.0	7.8	5.6	1000	CH ₃ COOH
c13	KMnO ₄	11.0	7.8		500	Valeric acid
c14	KMnO ₄	11.0	7.8		1000	Valeric acid

9 and 10 cold neutral permanganate

11 and 12 hot neutral permanganate

13 and 14 alkaline permanganate

TABLE 3

RESULTS OF ACID PERMANGANATE

No. of run	Oxidizer used	Grams used	Percent excess	Grams acid	C.C. H ₂ O	Yield in % theoretical
15	KMnO ₄	6.10		6.00	250	0.00
16	KMnO ₄	6.10		6.00	500	8.50
17	KMnO ₄	6.10		6.00	1000	9.80
18	KMnO ₄	6.44	5.50	7.70	500	16.60
19	KMnO ₄	7.00	14.70	7.35	500	18.00
20	KMnO ₄	7.50	23.00	7.70	500	16.10
21	KMnO ₄	7.00	14.70	7.35	1000	16.40

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TABLE 4

RESULTS OF ADDING $K_2Cr_2O_7$ TO GERANIOL

No. of run	Oxidizer used	Grams used	Percent excess	Grams acid	C.C. H_2O	Yield in % theoretical
22	$K_2Cr_2O_7$	10.00	0.2	13.1	100	10.9
23	$K_2Cr_2O_7$	10.00	0.2	13.1	200	14.7
24	$K_2Cr_2O_7$	10.00	0.2	13.1	500	15.0
25	$K_2Cr_2O_7$	10.50	6.3	13.1	200	18.0
26	$K_2Cr_2O_7$	11.00	11.9	13.1	200	20.0
27	$K_2Cr_2O_7$	11.50	16.5	13.1	200	23.2
28	$K_2Cr_2O_7$	12.00	21.6	13.1	200	22.8



THE BEST PROCESS OF OXIDATION

The best complete process for the oxidation of geraniol may be deduced from the data and results given in the tables, but should be directed as follows:-

11.5 grams of potassium bichromate are dissolved in 200 grams of water containing 13 grams of sulphuric acid. 15 grams of geraniol are used and the potassium bichromate solution added to them gradually, with constant, vigorous stirring, in the course of about an hour and thirty minutes. The reaction-mixtures should never be allowed to go above 20 degrees centigrade. When the potassium bichromate has all been added the whole is made slightly alkaline with sodium carbonate and then distilled in a vacuum at a pressure of 5 to 7 mm. At this pressure the water and geraniol come over together. The oil separates and floats on top of the water, from which it can readily be separated. More water is

poured onto the pasty mass and it is again vacuum distilled. The geranial and water are distilled over and separated as before. Great care must be exercised in the vacuum distillation because at such a low pressure a very little vapor will occupy a tremendous amount of space and will invariably cause bumping. The bumping may, as it often does, become so violent as to bump some of the chromium salts over and they impart a very dark green color which can only be removed by another vacuum distillation. This means a great loss in the product and also in time. The vacuum distillations were all made with a Cenco-Nelson water cooled pump.

For the commercial application of this procedure a cast iron kettle, to which stirring paddles are attached, will be necessary. The potassium bichromate solution may be added in one of any number of ingenious methods. Since the solution is made only slightly alkaline

almost any good still will fit the bill. It may not be obvious, but it is of primary importance to have a good vacuum, because decomposition takes place at high temperatures. It is therefore necessary to use a reliable vacuum pump such as the Lammert and Mann two phase water cooled pump. The receiver may be any modern rearrangement of the Florentine flask. The water may be readily separated from the geranial from time to time with one of these receivers without losing the vacuum or stopping the distillation.

ESTIMATION AND DETECTION OF GERANIAL

The best method for the estimation of ger-anial is the method known as the bisulphite method. It was first introduced in 1890 by Schimmel and Company for the cinnamic aldehyde assay of cassia oil. At present, it plays an important role in the assay of oils containing cinnamic aldehyde or geranial. The method depends on the property of both cinnamic aldehyde and geranial to dissolve in hot concentrated sodium bisulphite solution with the formation of sulphonate, hence can be abstracted quantitatively from the oils, whereas the non-aldehyde constituents remain undissolved. The amount of dissolved oil reveals its aldehyde contents.

For this determination a special glass flask is used. It has a capacity of about 100 c.c., is provided with a neck about 13 c.c. long, the inner diameter of which is 8 mm. and which is calibrated into $\frac{1}{10}$ c.c. The entire neck of the flask has a

capacity of about 6 c.c. The zero point of the scale is placed slightly above the transition point of the flask into the neck.

By means of a pipette 10 c.c. of oil are transferred to the flask and an equal volume of 30 percent sodium acid sulphite solution is added. Care should be taken that the solution does not contain too much free sulphurous acid since this retards the reaction. If necessary, the solution should be neutralized somewhat by the addition of sodium carbonate. The mixture is shaken and the flask placed in a boiling water bath. After the solid mass has become liquid more acid sulphite solution is added until the flask is at least three quarters full, the mixture being constantly heated and shaken. The solution is heated until no more solid particles are visible and the odor of aldehyde has disappeared. When the clear oil floats upon the salt solution, flask and contents are allowed to cool and sufficient acid sulphite solution is added until the



oily layer is well within the neck of the flask. Should drops of oil adhere to the flask these are induced to rise into the neck by gentle tapping and rotation of the flask. The number of c.c. of oil is read off and by deducting this number from ten, the aldehyde contents in percent by volume is ascertained by multiplying the resultant with ten. In order to obtain the percentage by weight the number obtained is multiplied with the specific gravity of the aldehyde in question and the product divided by the specific gravity of the oil.

In the attempts that were seemingly unsuccessful it was necessary to make a qualitative test to ascertain whether or not there was any geranial present. The method of procedure was as follows:-

The reagent consists of 10 grams of mercuric sulphate dissolved and made up to 100 c.c. with 25 percent sulphuric acid. 2 c.c. of the substance are shaken in a corked bottle with 5 c.c. of the reagent, and the color is observed at

once and also is retained after standing ten minutes. Smaller quantities may be tested on a tile.

The results of this test are: Geranial a bright red color on shaking, which disappears leaving a whitish compound floating on the aqueous liquid. This test may be used for several other compounds of the terpene series each giving its characteristic color test.



